

Molecular Building Blocks Made of Diamonds



DIAMOND, a form of crystalline carbon, has long been treasured as a precious jewel. However, for many years, tiny diamond particles, equivalent to a billionth of a billionth of a carat, have plagued oil workers when the particles clump together and clog pipelines. These particles, called diamondoids, can be found in crude oil at concentrations up to thousands of parts per million. Similar diamondlike carbon nanoparticles occur in meteorites, interstellar dust, and protoplanetary nebulae. High-explosive detonations have produced much larger, less pure diamond nanoparticles.

A team of Livermore researchers led by physicist Trevor Willey is helping to transform diamondoids from pesky pipeline sludge and astronomical curiosity into building blocks for new materials. The researchers are also investigating the microscopic particles' fundamental electrical properties, which could lead to their use in electronic devices.

Diamondoids comprise one to many units of the compound adamantane (from "adamas," the Greek word for diamond). First discovered in 1933, adamantane is the smallest cage structure of the diamond crystalline lattice, consisting of 10 carbon atoms and 16 hydrogen atoms. A single adamantane molecule terminates in atoms of hydrogen. However, when the units repeat billions of times in three dimensions, the carbon atoms of other adamantane cages replace the terminal hydrogen atoms, forming the bulk diamonds used in jewelry and industry.

Adamantane, diamantane (two units of adamantane), and triamantane (three units) are referred to as lower diamondoids because each has only one shape. The "higher" diamondoids—those with more than three linked adamantane units—can assume several possible shapes. The lower diamondoids can be easily synthesized, but chemical synthesis of larger diamondoids has proven impossible except for one form of tetramantane (four units of adamantane).

Diamondoids as Semiconductors

Livermore's diamondoid work is an outgrowth of semiconductor research that began in the mid-1990s with funding from the Laboratory Directed Research and Development Program. A semiconductor is a crystalline solid exhibiting electrical properties between those of metals and insulators. In that initial project, Willey worked with physicist Tony van Buuren and postdoctoral researcher Christoph Bostedt (now at the Technical University of Berlin) to determine how quantum confinement affects the electronic properties of silicon and germanium.

Quantum confinement, which restricts an electron's motion, occurs in a minute sample, typically 10 nanometers or less. The Livermore team discovered that quantum confinement increases the band gap (the energy required for an outer electron to become conductive) in silicon and germanium as molecule size decreases. The band gap is important because it indicates which wavelengths, or colors, of light a semiconductor can absorb or emit. By adjusting, or tuning, the band gap, researchers can design applications from efficient photovoltaic cells (which convert sunlight into electricity) to color-tunable lasers and light-emitting diodes.

In 2003, the team began examining carbon, specifically nanodiamonds obtained from high-explosive detonation residue. In the periodic table of elements, carbon (diamond) is in the same column (called Group IV) as silicon and germanium. Elements grouped in columns often have similar chemical and electronic properties, so carbon might behave like other semiconductor materials.

However, the smallest diamondoids the physicists could isolate measured 2 to 3 nanometers—too large for observing quantum confinement and other changes in electronic structure. Moreover, the surface of the recovered diamondoids resembled buckyballs, 60-atom molecules whose properties are more like graphite

(another form of crystalline carbon) than diamond. Ideally, the researchers wanted samples that terminated in hydrogen atoms to preserve the diamondoid characteristics.

The Livermore research effort took an unexpected turn when Chevron scientists, who had been studying clogged oil pipelines in the Gulf of Mexico, published a paper in the January 3, 2003, issue of *Science*. The paper described the discovery of higher diamondoids ranging from less than 1 to about 2 nanometers (that is, with 2 to 11 adamantane units). These diamondoids, presumably created deep underground with crude oil, seemed perfect for the Livermore research effort: They were less than 2 nanometers, the size predicted for observing quantum confinement effects in diamond, and they terminated in hydrogen atoms.

Van Buuren contacted the Chevron researchers, and the Livermore team soon began collaborating with Molecular Diamond Technologies, a business unit established by Chevron to research and commercialize diamondoids. "With the samples from Molecular Diamond Technologies, we could study the evolution of the electronic structure in carbon as a function of size," says Willey. He notes that methane (natural gas), a single carbon atom surrounded by four hydrogen atoms, and other small hydrocarbons have properties very different from diamond. "Diamondoids bridge the gap between small hydrocarbons and bulk diamond," says Willey. "Their availability opens a wealth of possibilities in nanoscience and technology."

Five researchers from the Chemistry, Materials, Earth, and Life Sciences Directorate are currently involved in the diamondoid research effort, which is funded by the Department of Energy's Office of Basic Energy Sciences. In addition to Chevron, collaborators include the Technical University of Berlin; Stanford

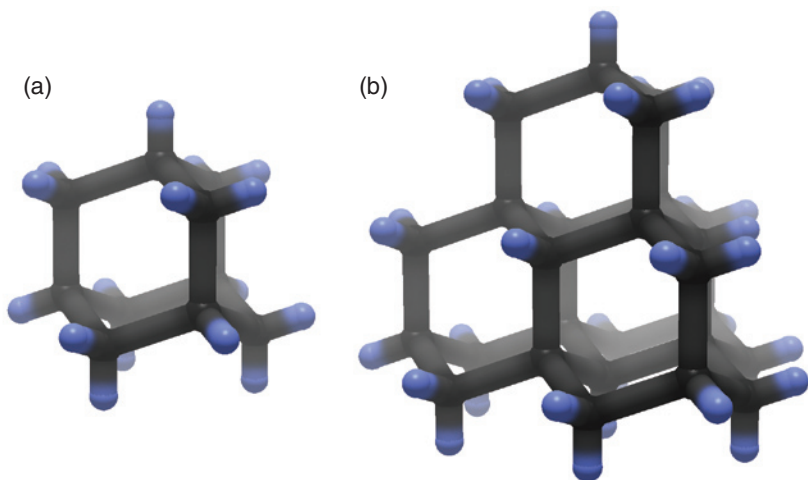
University; Justus-Liebig University in Giessen, Germany; and several national laboratories.

Using soft-x-ray absorption and emission spectroscopy, the research team found that the electrical properties of diamondoids differ from those of other semiconductor nanocrystals. In silicon and germanium, for example, the conduction band minimum (the lowest energy level at which a semiconductor allows electrical conduction) increases as the molecule's size decreases. With diamondoids, the conduction band stays constant, presumably because hydrogen atoms are present.

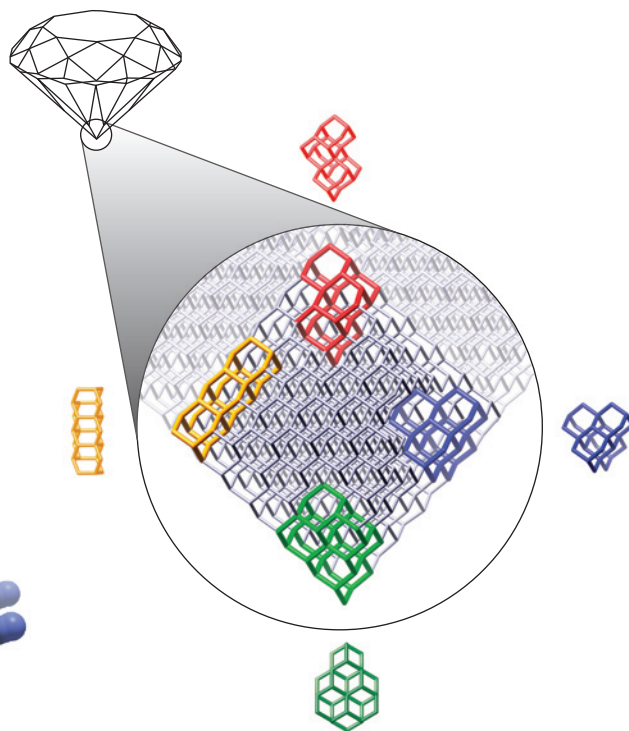
"That finding is a big surprise because carbon is in the same column as silicon and germanium," says Willey. "The lowest unoccupied state is at the surface of the diamondoid, where calculations and experiments show the electron gets emitted spontaneously." Scientists refer to such molecules as having negative electron affinity. This property makes diamondoids ideal for many nanotechnology applications that require efficient electron emission.

Building Monolayers

As part of this project, Willey is building diamondoid monolayers, single layers of diamondoid molecules attached to a film of inert metal, typically gold. Monolayers are joined by

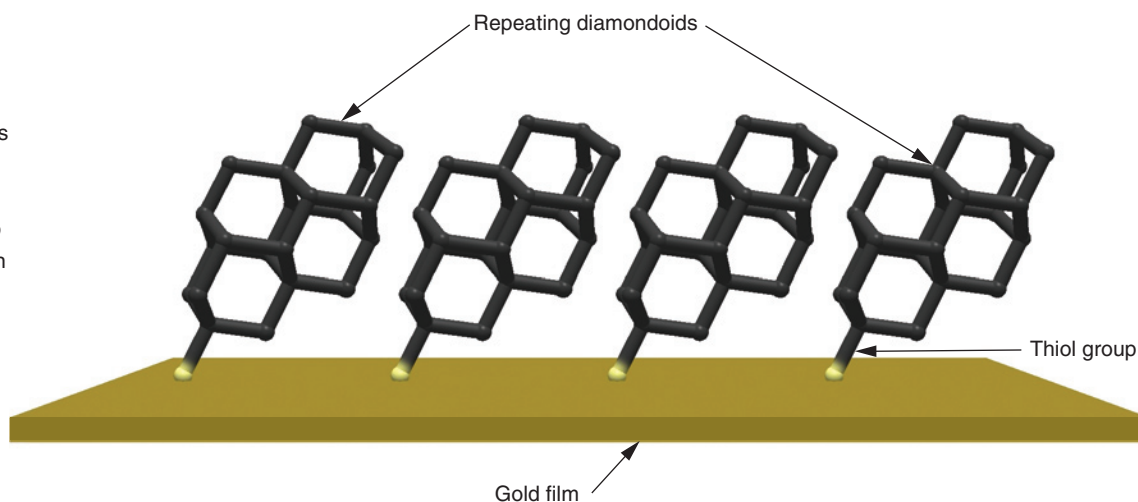


(a) Adamantane consists of 10 carbon (black) and 16 hydrogen (blue) atoms. Diamondoids form when multiple adamantane units, or cages, join together. (b) Pentamantane (five units) can be viewed as one adamantane cage surrounded by four additional cages.



Diamond's crystalline structure is made of repeating units of adamantane. The colored molecules depict four configurations of pentamantane, a diamondoid composed of five adamantane cages. (Courtesy of Chevron Corporation.)

One layer of diamondoid molecules can be attached to a film of inert metal, typically gold, by replacing a hydrogen atom with a thiol group (one sulfur atom and one hydrogen atom). The diamondoid monolayer shown here is tetramantane.



replacing a hydrogen atom with a thiol group (one sulfur atom and one hydrogen atom). Thiol groups are used in building monolayers of hydrocarbons, which Willey previously researched.

Building monolayers is the first step toward using diamondoids as molecular building blocks for nanotechnology components. Other carbon or hydrogen atoms could be replaced with desirable chemical groups, for example, to attach diamondoids to different surfaces, join diamondoids to build precise and rigid molecular-scale objects, or link diamondoids to biological or other macromolecules.

The Livermore team has characterized the monolayers using synchrotron sources of very bright x rays, including the Advanced Light Source at Lawrence Berkeley National Laboratory, Stanford Synchrotron Radiation Laboratory, and several facilities in Germany. In studies with near-edge x-ray absorption fine-structure spectroscopy, they found that the orientation of diamondoids within each monolayer depends on both the location of the thiol group (the specific hydrogen atom the thiol group replaces) and the diamondoid composing the monolayer. To date, the team has formed monolayers of adamantane, diamantane, triamantane, and tetramantane. When excited by ultraviolet photons, these monolayers generate large emissions of electrons, which are also monoenergetic. That is, most of the electrons lie within a single energy peak, which has an energy distribution width of less than 0.5 electronvolts.

From Microscopes to Pharmaceuticals

Within a few years, diamondoids could be used in products ranging from electron microscopes to pharmaceuticals. Because diamondoids can absorb substantial heat without breaking down, they could be used as fuel additives and material coatings. As electron emitters with a narrow energy distribution, they could

improve electron microscopes, which usually have a broad and thus inefficient energy distribution. With their high efficiency, they might also decrease the energy consumption in field-emission flat-panel displays.

Because diamondoids are inert, nontoxic, rigid, and available in various shapes and sizes, they may work in biological applications as well. “The pharmaceutical industry is excited about the possibilities,” says Willey. An adamantane derivative called aminoadamantane is used in drugs designed to fight viruses and reduce the effects of Alzheimer’s and Parkinson’s diseases.

Another potential application is in polymers and material coatings. Many polymers use hydrocarbon building blocks—floppy molecules that produce a malleable product. In contrast, diamondoids are rigid at the molecular level, leading to tunable polymer properties. Diamond monolayers are potentially superior to current substrates used to grow synthetic diamonds. “Producing perfect diamonds has been a Holy Grail for many chemists,” says Willey.

In his current research effort, Willey is determining the three-dimensional orientation of the diamondoids comprising monolayers. He also plans to build monolayers from higher diamondoids. In the growing world of nanotechnologies, diamondoids will likely play an important role as adaptable building blocks for new materials and products.

—Arnie Heller

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